

CERAMIC SPHERES DERIVED FROM CATION EXCHANGE BEADS

F. W. Dynys

NASA

Glenn Research Center

21000 Brookpark Rd.

Cleveland, OH 44135

ABSTRACT

Porous ZrO_2 and hollow TiO_2 spheres were synthesized from a strong acid cation exchange resin. Spherical cation exchange beads, polystyrene based polymer, were used as a morphological-directing template. Aqueous ion exchange reaction was used to chemically bind $(\text{ZrO})^{+2}$ ions to the polystyrene structure. The pyrolysis of the polystyrene at 600°C produces porous ZrO_2 spheres with a surface area of $24\text{ m}^2/\text{g}$ with a mean sphere size of $42\text{ }\mu\text{m}$. Hollow TiO_2 spheres were synthesized by using the beads as a micro-reactor. A direct surface reaction between titanium isopropoxide and the resin beads forms a hydrous TiO_2 shell around the polystyrene core. The pyrolysis of the polystyrene core at 600°C produces hollow anatase spheres with a surface area of $42\text{ m}^2/\text{g}$ with a mean sphere size of $38\text{ }\mu\text{m}$. The formation of ceramic spheres was studied by XRD, SEM and B.E.T. nitrogen adsorption measurements.

INTRODUCTION

As gas turbine technology advances, demand for efficient engines and emission reduction requires a further increase in operating temperatures. Combustion temperatures are currently limited by the temperature capability of the engine components. The existing thermal barrier coating (TBC) technology does not provide sufficient thermal load reduction at 3000°F (1649°C) operating conditions. Advancement in thermal barrier coating technology is needed to meet this challenging temperature goal.

One concept for improving TBC effectiveness is to design TBC systems which incorporate a layer that reflects or scatters photon radiation. Efficient scattering of photon radiation can be achieved using porous structures. The refractive index mismatch between the solid and pore, the pore size and pore density can be engineered to efficiently scatter photon radiation.[1] Porous

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coatings can be created from hollow ceramic spheres. Diverse ceramic processing techniques have been developed to fabricate hollow spheres: nozzle-reactor systems[2], templating [3] and emulsion/phase separation techniques[4]. Process selection depends upon the required particle size, pore size and chemical composition.

The objective of this study was to develop a process to fabricate ceramic spheres containing 1-5 μm size pores. A straightforward templating process that requires no special processing equipment to fabricate ceramic spheres was investigated. It has been reported that spherical organic anion exchange beads act as a morphological-directing template to produce porous SiO_2 spheres and hollow spheres of WO_3 and FeO . [5-7] This work focuses on utilizing a polystyrene base cation exchange resin to fabricate ZrO_2 and TiO_2 spheres. Porous structures utilizing ZrO_2 and TiO_2 are important in applications for TBC and photonics. This paper describes two separate processes utilizing cation exchange beads. One process utilizes the ion exchange process to template the polymer structure and the other process utilizes the beads as a micro-reactor to deposit a coating on the bead surface.

EXPERIMENTAL

A strong acid cation exchange resin, Dowex 50x4, was purchased from Aldrich Chemical. The exchange resin contained a 4% cross-linker concentration of divinylbenzene. The morphology of the particles were spherical with a wet sieved mesh size of -200 to +400. Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%) was used for the exchange reaction. Minimal time for ion exchange reaction was 24 hrs. in a solution of 0.1–0.3 M zirconyl chloride. Exchange media was separated from the liquid by filtering, proceeded by rinsing the beads with water and a final wash using isopropanol. The treated beads were dried at room temperature. ZrO_2 spheres were formed by calcining the treated beads in air using a heating rate of 6 $^\circ\text{C}/\text{min}$ and soaked for 6 hrs. at 600 $^\circ\text{C}$.

Hollow spheres of titania were made by reacting titanium isopropoxide with absorbed water contained within the ion exchange beads. Titanium isopropoxide (97%) was obtained from Alfa Aesar. An emulsion technique was used to fabricate the spheres. Prepared suspensions contained 12.5 wt. % Dowex 50x4, 0.5 wt. % Span 80 and 87 wt. % 2,2,4-trimethylpentane. The exchange media was suspended by agitation using a magnetic stir bar. A Titanium isopropoxide solution containing 22 vol. % titanium isopropoxide, 73 vol. % isopropanol and 5 vol. % 2,4-pentanedione was dripped into the suspension. The spheres were separated from the liquid by filtration. Coated beads were dried at room temperature in air. The same calcination schedule was used as stated above for ZrO_2 .

The morphological characteristics and particle size of the ceramic spheres were characterized by scanning electron microscopy (SEM). The size distribution of the spheres were determined from SEM micrographs. Image analysis software, Image Pro Plus, was used for particle size measurements. The surface area of the

fabricated spheres were measured by nitrogen gas adsorption and analyzed using the 5 point Brunauer-Emmett-Teller method.

The amorphous and crystalline structures were determined by x-ray diffraction. The x-ray diffractometer was equipped with a Cu K_{α} source with a wavelength of 0.1540 nm. The operating conditions were 45 KV and 40 mA. Scans were conducted at 3°/min with a sampling interval of 0.02°.

RESULTS AND DISCUSSION

Porous ZrO_2 Spheres

Porous ZrO_2 spheres were fabricated by templating the polystyrene structure of the Dowex 50x4 resin. Figure 1 shows an image of ZrO_2 microspheres produced using this method. The particle size distribution of the ZrO_2 spheres and the treated $ZrOCl_2$ beads is shown in Figure 1.

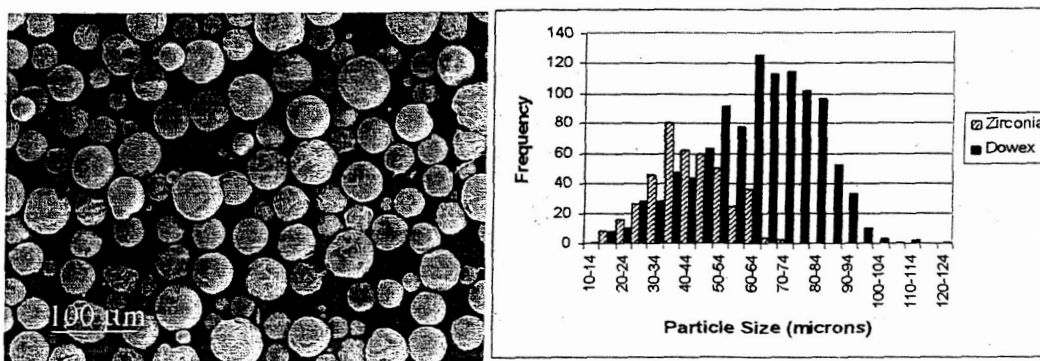


Figure 1. SEM image of spherical ZrO_2 particles and particle size distributions.

The dried $ZrOCl_2$ treated beads have a broad bead size range of 15 to 125 μm with a mean bead size of 62 μm . Calcination of the $ZrOCl_2$ treated beads results in a size reduction and a narrower ZrO_2 sphere distribution; the mean size decreases to 42 μm and exhibits a narrower diameter range of 10 to 75 μm . The measured surface area of the ZrO_2 spheres was 24 m^2/g . ZrO_2 has three crystalline phases. The monoclinic phase is thermodynamically stable phase <1170 °C, tetragonal and cubic phases are stable at higher temperatures. X-ray diffraction (XRD) of the calcined powder shows that 600 °C calcination is sufficient to crystallize ZrO_2 in the tetragonal form, as shown in Figure 2. It is not uncommon for metastable ZrO_2 phases to form during powder synthesis. Most amorphous ZrO_2 precursors crystallize into the tetragonal phase first and then transform to the monoclinic phase at higher calcinations temperatures.[8]

Successful fabrication of the ZrO_2 spheres is strongly dependent on the calcination heating rate and the ion exchange time. A heating rate $\geq 6^\circ C/min$ and ion exchange time ≥ 18 hrs. was established to produce intact ZrO_2 spheres.

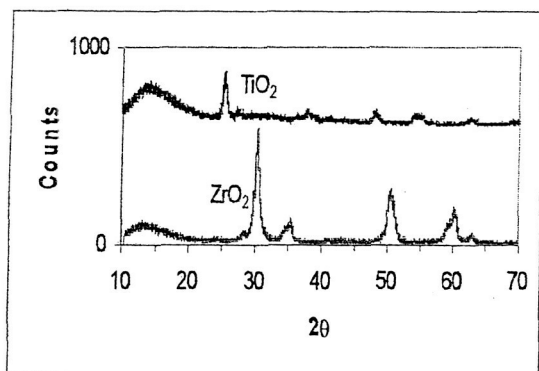


Figure 2. XRD pattern of ZrO_2 and TiO_2 spheres.

A slow calcination schedule ($<1^\circ\text{C}/\text{min}$) produces a large population of broken spheres and partially collapsed spheres. It was observed from the slow calcinations that a small population of ZrO_2 spheres remain undamaged. This indicated that a dependent process parameter existed. Heating rates of 1, 2, 3 and $6^\circ\text{C}/\text{min}$ were evaluated. It was found that a $6^\circ\text{C}/\text{min}$ heating rate produced nearly a 100% population of intact ZrO_2 spheres.

The lower heating rates tried did not

significantly increase the population of intact ZrO_2 spheres. These results differ from Bourlinos et al. They reported a $1^\circ\text{C}/\text{min}$ heating rate was sufficient for sphere fabrication using anion exchange polystyrene beads. It is also observed at the $6^\circ\text{C}/\text{min}$ rate that the polystyrene beads ignite.

The treated beads emitted luminous energy when the furnace temperature was greater than 500°C . It is believed that the combustion inhibits the collapse of the ceramic sphere. Localized temperature rise aids in sintering which stabilizes the ceramic structure from collapsing. Significance of the temperature rise to the crystallization of the tetragonal phase has not been determined.

Once the calcination schedule was established, the ion exchange time was investigated. This was done to find if different morphological structures could be attained at different ion exchange times. Times of 4 hrs, 8 hrs, 18 hrs, 24 hrs, 48 hrs and 72 hrs were tried. It was found that a minimum treatment time of 18 hrs. was needed to produce intact ZrO_2 spheres. The 4 and 8 hrs. treatments produce a large population of collapsed or defective spheres at a heating rate of $6^\circ\text{C}/\text{min}$. No morphological changes were observed for treatment times >18 hrs.

The morphological structure of the ZrO_2 sphere replicates the polystyrene template. Two different surface morphologies are observed. A minor population of spheres exist that exhibit a surface appearance consisting of a wrinkled ZrO_2 structure integrated with coarse pores as shown in Figure 3a. It is not known whether the polymer structure is different or whether the local calcination conditions cause this morphological structure. The normal sphere population exhibits a smooth surface appearance with a fine pore size. The internal structure of the spheres consist of a outer spherical shell of ZrO_2 that encapsulates a porous sphere of ZrO_2 , as shown in Figure 3b. The shell thickness is estimated to be $\leq 0.5 \mu\text{m}$ from SEM images. The fragile nature of the shell suggests that it is weakly bonded to the inner sphere. The inner sphere is porous and contains thin sheets of ZrO_2 separated by asymmetrical pores, as shown in Figure 3c. Asymmetrical pores are approximately $0.5\text{-}2 \mu\text{m}$ in width, sufficient in size to scatter radiative

heat. The ZrO_2 sheets appear to have a preferred growth direction towards the sphere center.

Bourlinos et al reported hollow sphere fabrication from anion exchange media. Results show that the ion exchange process using a cation exchange resin was incapable of fabricating hollow ZrO_2 spheres. A core/shell structure has been reported for porous SiO_2 spheres by Tosheva et al. Further details are needed on the polystyrene structure to elucidate the formation of the core/shell structure.

Initial sintering data shows that the ZrO_2 spheres begin to densify around 1250°C . Characterization of the internal pore structure during sintering has not been completed. Retaining a stable internal pore structure is important for high temperature coating applications.

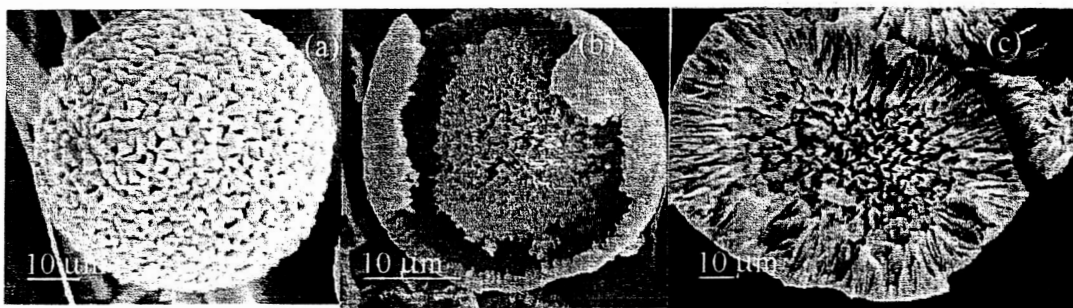


Figure 3. Morphological structure of ZrO_2 spheres.

Hollow TiO_2 Spheres

Hollow TiO_2 spheres were synthesized by a surface reaction of titanium isopropoxide with internally absorbed water in the Dowex 50x4 beads, as shown in Figure 4. The beads act as a micro-reactor forming a hydrous TiO_2 coating. The TiO_2 spheres show wrinkles or folds on the surface. SEM examination revealed that the rough surface formation results from the coating process and not from the pyrolysis of the polystyrene. The roughness suggests that the coating process involves an uncontrolled hydrolysis reaction of the titanium isopropoxide. The used of acetylacetone as a chelating agent appears not to be effective in reducing the hydrolysis and condensation reaction rate. Wall thickness of the hollow spheres was estimated to be $1\text{--}3\ \mu\text{m}$. Average TiO_2 sphere size was $38\ \mu\text{m}$ with a range of 10 to $60\ \mu\text{m}$. Pore size resembles the sphere size distribution. The average size of the hydrous coated Dowex 50x4 beads was $40\ \mu\text{m}$. TiO_2 spheres exhibit a small amount of shrinkage from the parent population. The measured surface area of the TiO_2 spheres was $42\ \text{m}^2/\text{g}$. TiO_2 exhibits three crystalline phases: rutile, anatase and brookite. All three phases occur in nature, rutile has been identified as the thermodynamically stable form of TiO_2 . Brookite and anatase transform to rutile at temperatures $>400^\circ\text{C}$. Phase identification by x-ray diffraction matched anatase, as shown in Figure 2. The anatase phase is poorly crystallized. Anatase formation is commonly observed in sol-gel preparation of TiO_2 derived from titanium alkoxides.

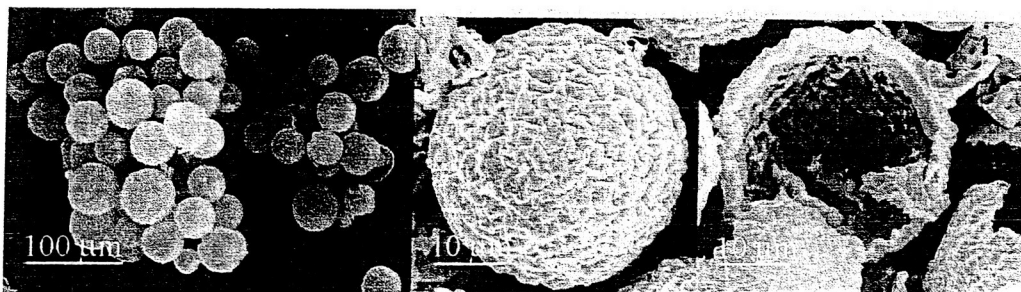


Figure 4. SEM images of hollow TiO_2 spheres.

The objective of forming TiO_2 spheres was to prove the micro-reactor concept. The success of the process indicates that it should be capable of forming other oxides, e.g., ZrO_2 from zirconium alkoxides. A smaller bead size Dowex 50x4 was not commercially available to produce a smaller pore size. Replacing the Dowex 50x4 beads with hydrophilic polystyrene beads is a viable option for smaller pores. Sub-micron to micron size polystyrene beads are available.

SUMMARY

Fabrication of porous ZrO_2 spheres and hollow TiO_2 spheres was achieved by templating using a polystyrene base cation exchange resin. Ion exchange reaction using aqueous chemistry was successfully used to fabricate porous ZrO_2 spheres. ZrO_2 spheres contained internal pores that are 0.5-2 μm in size. Pore size is suitable for efficient scattering of visible and near infrared radiation. Calcination heating rate and ion exchange time were identified as critical parameters in forming fully intact ZrO_2 spheres. Hollow TiO_2 spheres were formed by using the polystyrene beads as a micro-reactor. Interfacial reaction between titanium isopropoxide and polystyrene bead produced a hydrous TiO_2 coated bead. Available Dowex 50x4 bead size regulated the internal pore size.

ACKNOWLEDGEMENT

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